Laser Heating and X-ray Microdiffraction: A Powerful Tool to Study Melting of Metals at Extremely High Pressures and Temperatures

D. Errandonea,[1,2] M. Somayazulu,[2] D. Häusermann,[2] H.K. Mao[3]
[1]Departamento de Física Aplicada-ICMUV, Universitat de València,
Edificio de Investigación, Burjassot, Valencia, Spain
[2]Carnegie Institution of Washington (CIW), Washington, DC, U.S.A.
[3]Geophysical Laboratory, CIW, Washington, DC, U.S.A.

Introduction

Recent developments in synchrotron-based high-pressure experiments have allowed us to investigate the nature of materials directly under the extreme high-pressure and high-temperature conditions that exist within deep planetary interiors. By using the laser-heating system available at the HP-CAT beamline at the APS and angle-dispersive x-ray microdiffraction, we have studied the melting properties of transition metals at high pressure.

Melting under compression is an intriguing subject. It can be observed in a laser-heated diamond anvil cell (DAC) and in shock experiments. Also, many attempts have been made to theoretically predict the melting curves of different metals. Still today, these three methods yield very different results.

Tantalum (Ta) and tungsten (W), two of the metals with the highest melting temperature (T_m) at 1 bar, remain stable in the bcc structure up to megabar pressures. These two characteristics allow melting to be studied over a wide range of pressures without the complication of solid-solid structural transitions, thereby making Ta and W excellent candidates for improving the understanding of melting. Previous studies of the high-pressure melting of Ta showed large discrepancies (e.g., at 25 GPa, experiments observed T_m = 3500 ±100K, and theory predicts T_m = 4500K), which are summarized in Fig. 1. These disagreements, which include even the melting slope at 1 bar, emphasize the need for a precise experimental study of the melting behavior of transition metals under compression. Accurate measurements of the melting of Ta and W in a pressure-temperature (P-T) range up to 50 GPa and 4000K are reported on here. These reliable experiments were carried out at HP-CAT beamline station 16-ID-B. A small slope for the melting curve of Ta and W is estimated, and an explanation for this fact is given by assuming a vacancy model for the melting process.

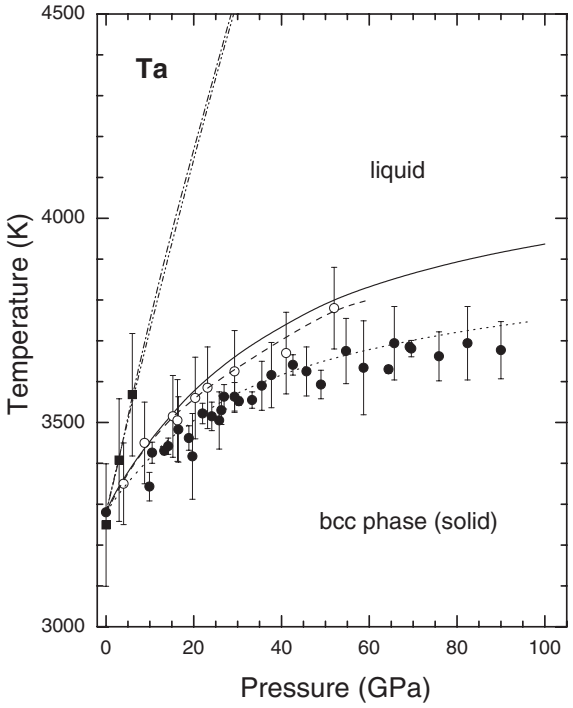

FIG. 1. Melting curve of Ta. Experimental data: open circles represent present work, solid circles represent Ref. 1 data, and solid squares represent Ref. 2 data. The single-dotted/dashed line illustrates the melting curve calculated in Ref. 3. The double-dottted/dashed line shows the Lidenmann law's estimates [4]. The large-dashed line fits the present melting data, and the small-dashed (may look dotted) line fits the data reported in Ref. 1. The solid line is the melting curve calculated from assuming the vacancy model for the melting process.

Methods and Materials

Commercial samples of 99.9% purity were used to perform the studies reported on here. Angle-dispersive x-ray microdiffraction measurements under high pressure and high temperature were performed in a double-sided, laser-heated, symmetric DAC at HP-CAT beamline station 16-ID-B. A double-crystal branching monochromator was used to produce a monochromatic x-ray beam with a wavelength λ of 0.3738 Å. The monochromatic x-ray beam was focused down to 10×10 μm

by using multilayer bimorph mirrors in a Kickpatrick-Baez configuration. Diffraction images were recorded with a MarCCD at a sample-to-detector distance of 258 mm.

Samples compressed from powder with a diameter of 30-50 μm and a thickness of 5 μm were loaded in stainless-steel or rhenium gaskets having a pressure chamber that is 100-150 μm in diameter and 30-μm thick. During sample loading, the samples were located at the center of the gasket hole; therefore, they avoided bridging the gasket. Dry sodium chloride (NaCl) was used as the pressure-transmitting medium, and it also acted as a thermal insulator between the sample and the diamond anvils. The ruby fluorescence technique was used to measure the pressure in the DAC, at room temperature (RT), from an unheated ruby chip placed 10 μm from the sample. The diffraction lines of NaCl were also used to estimate the pressure at RT and the thermal pressure induced by the heating. A typical x-ray diffraction spectrum at RT has at least four diffraction peaks associated with the sample.

Ta and W samples were double-sided laser-heated *in situ* by using the laser-heating system available at the HP-CAT beamline station, which consists of two identical Nd:YLF lasers (Photonics GS40, 85W, TEM_{01} mode, λ = 1053 nm). With this system, described in detail in Ref. 6, a 30- to 40-μm-diameter hot spot with a temperature gradient of <10K/μm was achieved at a temperature of about 4000K. Figure 2 shows a photo of the hot spot obtained in the Ta sample at a pressure of ≈8.65 GPa and a temperature of 3230 ±100K. The temperature from both sides of the heated samples was determined at an accuracy of ±100K by simultaneously measuring the thermal emission spectra of the sample from both sides of the DAC during the exposure of the charge-coupled device (CCD) [6]. These measurements were performed in the spectral range of 550-800 nm. Temperatures were determined by fitting the thermal radiation to the Planck radiation function.

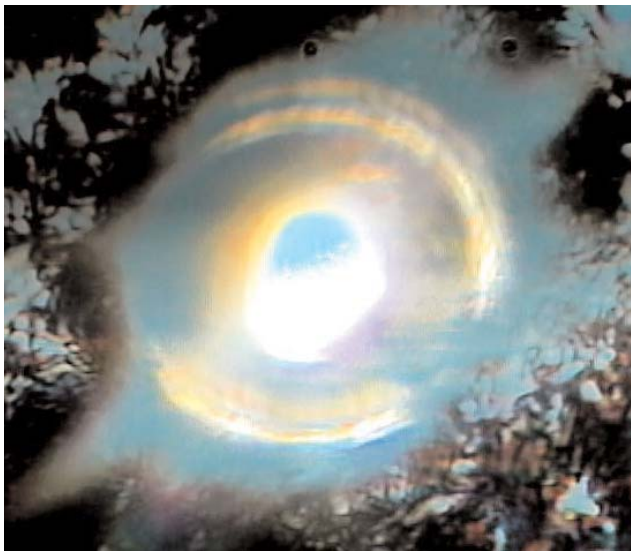

FIG. 2. 50-μm Ta sample laser-heated in a DAC at a pressure of 8.65 GPa and a temperature of 3230K.

One of the main advantages of the HP-CAT laser-heating system over the systems available in other synchrotron facilities is that in the HP-CAT system, the focusing optics are attached to the experimental sample stage. Therefore, when the sample is moved in order to position the x-ray beam at its center, the hot spot remains fixed on it. We estimated that the x-ray beam and the lasers from both sides were coincident within 3 μm. Then the 30- to 40-μm hot spot fully covered the 10-μm x-ray beam. In addition, a dual-imaging setup with two CCD cameras allowed us to visually observe the sample during the heating process and to check that the hot spot did not drift.

Results and Discussion

The melting behavior of Ta and W was studied by compressing the samples up to a desired pressure at RT and then heating them at constant load up to temperatures at which the x-ray diffraction peaks disappeared. When the sample was cooled to RT, no substantial change in pressure was observed with respect to the pressure measured before heating. The disappearance of all diffraction lines, the appearance of some diffuse broad scattering, and a substantial increase of the background were interpreted to indicate the onset of melting. After melting, upon cooling to RT, the diffraction lines of the bcc phase of Ta or W were recovered, which eliminated the chance that the diffraction peak's disappearance could have been related to any chemical decomposition of the sample. It is important to notice that in all the samples, the bcc phase was stable up to the onset of melting (i.e., there was not any phase of Ta or W that was different from bcc stability in the P-T range of this study). At 50 Gpa, we observed melting temperatures of 3800 ±100K and 4000 ±100K for Ta and W, respectively.

Figure 1 shows the melting results for Ta observed by us (open circles). Our measurements agree well with the melting curve determined by using the speckle method [1], but they are lower than the data determined by Fatteva and Vereschchagin using a piston-cylinder apparatus [2]. In Ref. 2, temperatures were estimated from the intensity ratios of thermal radiation measured in two narrow spectral ranges by assuming blackbody radiation. This method introduces large uncertainties in the temperature determination, which could easily explain the differences between the data reported in Ref. 2 and our data. From the present data and those of Ref. 1, we estimated a value for dT_m/dP of ≈24 ±2K/GPa for the slope of the melting curve of Ta at 1 bar. This value is nearly three times smaller than the values estimated from methods based on first-principle

calculations [3]. This fact raises concerns about the validity of calculating the pressure dependence of the melting properties of metals by using models based on parameters calculated at 1 bar. In Fig. 1, it can be also seen that melting estimates of Ta based on the Lindemann law are not compatible with the present experimental data at any pressure. This fact is not surprising, since the Lindemann law is an empirical law based on earlier experimental investigations of simple gases at low pressures. However, it does cast some doubt on the correctness of using the Lindemann law to calculate the melting behavior of transition metals under extreme P-T conditions.

The low rate increase of the melting temperature reported on here for Ta and W and reported on previously for other transition metals [1] can be understood when melting is discussed in terms of the generation of vacancies [5]. Within this framework, we calculated the melting curve of Ta by using the Clausius-Clapeyron equation:

$$\frac{\partial 1\mathrm{n}T_m}{\partial P} = \frac{\Delta V_m}{\Delta H_m},$$

where ΔV_m and ΔH_m are, respectively, the difference in molar volume and enthalpy of the solid and liquid coexistent phases at melting conditions. To integrate this equation, we need to know ΔV_m and ΔH_m as a function of pressure. For the pressure dependence of ΔH_m, we assumed that it is proportional to the vacancy formation enthalpy [5]. The pressure dependence ΔV_m can be estimated from data taken from the literature [1]. In Fig. 1, it can be seen that the predictions of the present vacancy model reproduce well the trend of the experimental results at every pressure.

By extrapolating the present results up to 3 Mbar, a melting temperature of 4800 ±300K is obtained. This temperature is way below the one determined in shock-wave experiments (T_m of >7000K) [7]. Direct temperature measurements in shock experiments require assumptions on the thermal and optical properties of the window material through which the sample is observed. The uncertainties may be on the order of 1000K. Another issue is the superheating effects due to the small time scale of the shock experiments, which can lead to a 2000K overestimation of T_m. These two facts could probably explain the differences between our prediction and the shock-wave data. Another question unanswered is whether there may be another factor at play in Ta, since the existence above 1 Mbar of a high-pressure and high-temperature phase in Ta is like the one proposed for molybdenum [8]. This scenario implies the existence of a triple point at the P-T conditions where the solid-solid boundary line intercepts the melting curve. Usually, such a triple point would produce a discontinuous change in the slope of the melting curve [9], which could make our data and calculations with the shock-wave data converge [8]. Clearly, a definitive understanding of the Ta phase diagram requires the extension of the laser-heating x-ray diffraction measurements reported on here up to megabar pressures.

In summary, we studied the melting of Ta and W up to 50 GPa and 4000K by combining the use of a micro x-ray beam and the laser-heating technique. The sharp x-ray distribution and the homogeneous temperature distribution achieved at HP-CAT beamline station 16-ID-B are critical for high P-T x-ray diffraction experiments in order to obtain quality data. The obtained results confirm previous DAC results that were in conflict with theoretical calculations and earlier piston-cylinder data. By interpreting the melting in terms of the generation of vacancies, we provide an explanation for the experimentally observed behavior.

Acknowledgments

Use of the APS was supported by the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences (BES), under Contract No. W-31-109-ENG-38. The HP-CAT beamline is supported by DOE BES, DOE National Nuclear Security Administration (NNSA), U.S. Department of Defense (DOD) Tank Automotive and Armaments Command (TACOM), and the W.M. Keck Foundation. D. Errandonea acknowledges financial support from the Ministerio de Ciencia Tecnología (MCYT) of Spain and the Universitat of València through the "Ramón y Cajal" program for young scientists.

This report was excerpted from "Melting of tantalum at high pressure determined by angle dispersive x-ray diffraction in a double-sided laser-heated diamond-anvil cell," J. Phys.: Condens. Matter **15**, 7635 (2003).

References

[1] D. Errandonea et al., Phys. Rev. B **63**, 132104 (2001).
[2] N.S. Fatteva and L.F. Vereshchagin, Sov. Phys. **16**, 322 (1971).
[3] Y. Wang et al., Phys. Rev. B **65**, 014104 (2002).
[4] F.A. Lindemann, Phys. Z. **11**, 609 (1910).
[5] S. Mukherjee, R.E. Cohen, and O. Gülseren, J. Phys.-Condens. Mat. **15**, 855 (2003).
[6] D. Errandonea et al., J. Phys.-Condens. Mat. **15**, 7635 (2003).
[7] J.M. Brown and J.W. Shaner, in *Shock Waves in Condensed Matter—1983*, edited by J.R. Asay, R.A. Graham, and G.K. Staub (Elsevier Science, New York, NY, 1984), p. 91.
[8] R.S. Hixson et al., Phys. Rev. Lett. **62**, 637 (1989).
[9] D. Errandonea, R. Boehler, and M. Ross, Phys. Rev. Lett. **85**, 3444 (2000).